J Appl Electrochem (2012) 42:305–317
DOI 10.1007/s10800-012-0395-3

ORIGINAL PAPER

Alkaline direct methanol fuel cell based on a novel anion-exchange composite polymer membrane

Chun-Chen Yang

Received: 22 November 2011 / Accepted: 18 February 2012 / Published online: 6 March 2012

Abstract The anion-exchange composite polymer membrane based on quaterized poly(vinyl alcohol)/poly(epichlorohydrin) (designated as Q-PVA/PECH) was prepared by a solution casting method and a quaternization process. The characteristic properties of the Q-PVA/PECH anion-exchange composite polymer membranes were investigated by scanning electron microscopy, thermal gravimetric analysis, micro-Raman spectroscopy, and AC impedance method. Alkaline direct methanol fuel cells (ADMFC) comprised Q-PVA/PECH anion-exchange composite polymer membranes were assembled and examined. Experimental results indicate that an alkaline DMFC employing an inexpensive non-perfluorinated Q-PVA/PECH composite polymer membrane shows excellent electrochemical performances. The peak power densities of the DMFC using 4 M KOH + 1 M CH_3OH, 2 M CH_3OH, and 4 M CH_3OH fuels are 17.22, 22.30, and 20.81 mW cm^{-2}, respectively, under ambient conditions. The Q-PVA/PECH composite polymer membrane appears as a viable candidate for use in an ADMFC.

Keywords Poly(vinyl alcohol) (PVA) · Poly(epichlorohydrin) (PECH) · Anion-exchange membrane · Quaternization · Direct methanol fuel cell

1 Introduction

Direct methanol fuel cells (DMFCs) are recently gaining much attention for their high potential applicability for electric vehicles, stationary applications, and portable power sources, such as cellular phones, notebook computers, etc. At present, alkaline DMFCs are being actively studied and a lot of progress has been made during the past few years [1–15]. However, the development of the DMFC has been hampered due to several major problems, which are slow methanol oxidation kinetics and incomplete electro-oxidation of methanol, the poisoning of adsorbed intermediate species on the Pt surface, the high methanol crossover through the solid-state polymer Nafion (Du Pont) membrane, and the high costs of the Nafion polymer membrane and Pt catalyst.

Recently, Yang [1, 2] synthesized crosslinked PVA composite polymer membrane for alkaline DMFC. A major benefit, the carbonation problem of alkaline DMFC can be greatly reduced using alkaline solid polymer membranes instead of an alkaline solution [12–15]. In addition, as we know, the anodic electro-oxidation of methanols in alkaline media shows much faster kinetics than that in acidic media [7]. Yang et. al. [16] prepared and studied alkaline poly (vinyl alcohol)/poly(epichlorohydrin) (PVA/PECH) blend polymer electrolyte and studied its electrochemical performance in Zn/air batteries. The ionic conductivity of the PVA/PECH polymer electrolyte was between 10^{-3} and 10^{-2} S cm^{-1} at room temperature. It was found that these PVA/PECH blend polymer membranes showed excellent mechanical strength, and chemical and electrochemical stability.

Interestingly, Xiong et. al. [17] studied a quaternized poly(vinyl alcohol) (here designated as QPVA) polymer membrane for DMFC application. The quaternary ammonium groups (i.e., $–N^+Me_3$ functional groups) were grafted onto the backbone of the PVA chain. The ionic conductivity of the QPVA anion-exchange polymer membrane was 7.34×10^{-3} S cm^{-1} in deionized water at 30 °C. More

C.-C. Yang (✉)
Department of Chemical Engineering, Mingchi University of Technology, New Taipei City 243, Taiwan, ROC
e-mail: ccyang@mail.mcut.edu.tw

recently, Xiong et. al. [18, 19] also prepared two organic–inorganic hybrid anion-exchange membranes based on QPVA/Tetraethoxylsilanes (TEOS) [18] and QPVA/chitosan [19]. These composite polymer membranes showed a high ionic conductivity of 10^{-3}–10^{-2} S cm^{-1} and a low methanol permeability of 5.68×10^{-7}–4.42×10^{-6} cm^2 s^{-1} at 30 °C. However, they did not show any electrochemical results of DMFC applications [17–19].

PECH [16] was used owing to its excellent mechanical strength and chemical properties. The addition of a stiff polymer of PECH into PVA polymer matrix is to reduce the glass transition temperature (T_g) and the crystallinity of the PVA polymer and increase the amorphous phases of polymer matrix, then to increase its ionic conductivity. As is known, when the stiff PECH polymer used as a solid plasticizer material is added to the soft PVA matrix, the swelling ratio of the PVA/PECH composite polymer membrane is effectively reduced. The thermal property, dimensional stability, and mechanical strength could also be improved.

In this study, we attempted to add a secondary PECH polymer into a PVA matrix to act as a solid plasticizer capable of enhancing the chemical and thermal properties, and mechanical strength of the PVA composite polymer membrane. The PVA/PECH composite polymer membrane was first obtained by directly blending PVA polymer and PECH polymer in DMSO under a stirring condition. The Q-PVA/PECH composite polymer membrane was then prepared through a quaternized process using glycidyltrimethyl ammonium chloride (GTMAC). An alkaline DMFC, composed of the air cathode loaded with MnO_2/BP2000 carbon inks on Ni-foam, the PtRu anode based on Ti-screen, and PVA/PECH composite polymer membrane, was assembled and investigated. The electrochemical characteristics of alkaline DMFC comprised Q-PVA/PECH composite polymer membrane were investigated by the linear polarization and galvanostatic methods; especially, for the peak power density of the alkaline DMFC at ambient conditions. For comparison, three KOH + 1, 2, and 4 M methanol concentrations were tested.

2 Experimental

2.1 Preparation of the Q-PVA/PECH anion-exchange membranes

PVA (Aldrich), PECH polymer (M.W. 700,000, Aldrich), GTMAC (Aldrich), dimethyl sulfoxide (DMSO), and KOH (Merck) were used as received without further purification. Degree of polymerization and saponification of PVA were 1,700 and 98–99%, respectively. The PVA/PECH composite polymer membrane was prepared by a solution casting method [8–10].

The appropriate quantities of PVA and PECH polymers (i.e., PVA:PECH = 5:0, 5:1, 5:1.5, 5:3, and 5:5 in weight ratios) were dissolved in DMSO under continuous stirring. The above resulting solution was stirred continuously at 65 °C for 10–12 h until the mixture became a homogeneous viscous solution. The resulting mixture solution was coated on a glass plate by a doctor-blade method. The thickness of the wet composite polymer membrane was between 0.020 and 0.040 cm. The glass plate with viscous PVA/PECH composite polymer sample was weighed again and then the excess DMSO was allowed to evaporate slowly at room temperature for several days. After evaporation of DMSO solvent, the glass plate with the composite solid polymer membrane was weighed again. The composition of PVA/PECH composite membrane was determined from the mass balance. The thickness of the dried composite polymer membrane was controlled in the range between 0.0090 and 0.0120 cm. The PVA/PECH composite membrane was further crosslinked by immersion in a solution of 5 wt% glutaraldehyde (GA, 25 wt% content in distilled (D.I.) water, Merck), 1.0 vol% HCl (as a catalyst), and acetone for the crosslinking reaction at 40 °C for 12 h. The crosslinked PVA/PECH composite polymer membrane was further quaternized by GTMAC, using GTMAC:KOH = 1:1 mol ratio at 65 °C for 4 h. After the quaternization process, or the so-called amination treatment, those Q-PVA/PECH anion-exchange solid polymer electrolytes (SPE) were washed with anhydrous ethanol and D.I. water several times; the Q-PVA/PECH SPEs were then dried and packed in a polyethylene (PE) bag for further testing [17–19]. Figure 1a shows the chemical structures of PVA, PECH, GPTMAC, and GA. Figure 1b shows a schematic diagram of the structure of Q-PVA/PECH anion-exchange composite polymer membrane.

2.2 Thermal, crystal structure, morphology analyses

Thermal Gravimetric Analysis (TGA) was carried out using a Mettler Toledo TGA/SDT 851^e system. Measurements were made by heating from 30 to 600 °C under a N_2 atmosphere at a heating rate of 10 °C min^{-1} with about 10 mg sample. The crystal structures of the Q-PVA/PECH composite polymer membranes were examined using a Philips X'Pert X-ray diffractometer (XRD) with Cu Kα radiation of wavelength $\lambda = 1.54056$ Å for 2θ angles between 10° and 70°. The surface morphology and microstructure of Q-PVA/PECH composite polymer membrane was investigated by a scanning electron microscope (SEM) (Hitachi S-2600H).

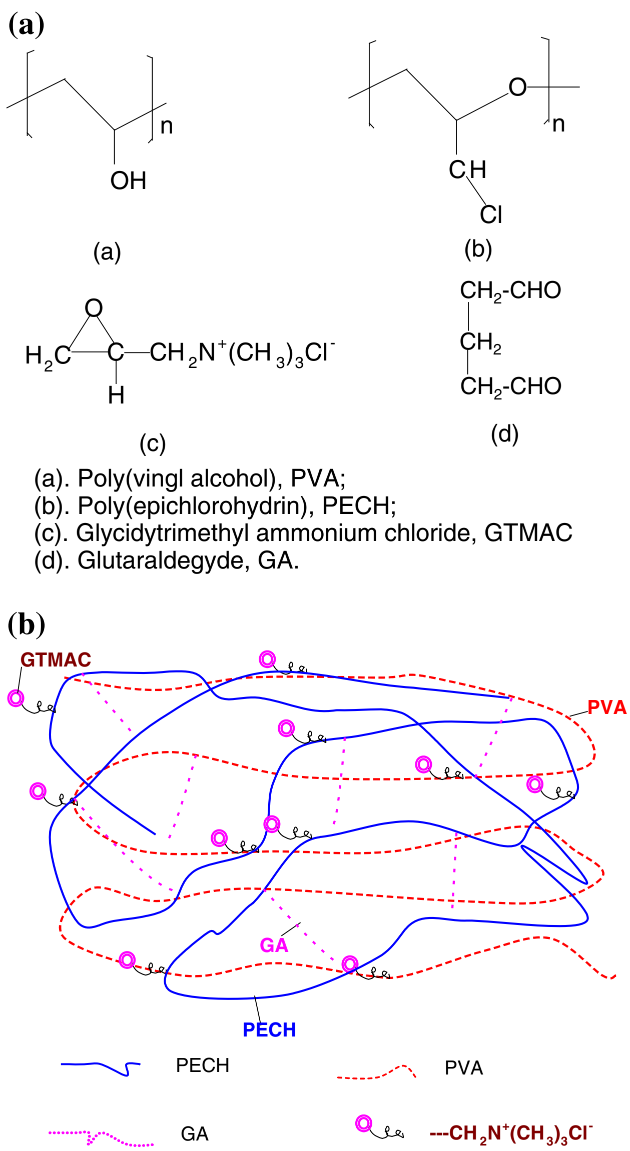

Fig. 1 **a** The chemical structures of PVA, PECH, GPTMAC, and GA; **b** a schematic diagram of a Q-PVA/PECH anion-exchange membrane

2.3 Liquid uptake and swelling ratios

Those weighed and dried QPVA/PECH composite polymer membranes (W_o) were immersed in D.I. water and 99 wt% CH_3OH, and maintained for 24 h at 25 °C until the equilibrium was established. The Q-PVA/PECH composite polymer membrane was taken out from the immersion bath and the excess surface water was carefully removed. The weight of the wet composite polymer membrane (W_1) was then determined again. The percent of H_2O absorption and swelling ratio was calculated from Eqs. 1 and 2 [1], respectively.

$$\text{Liquid uptake } (A\%) = \frac{W_1 - W_o}{W_o} \times 100 \tag{1}$$

$$\text{Swelling ratio } (S\%) = \frac{W_1 - W_o}{W_1} \times 100 \tag{2}$$

2.4 Ionic conductivity and methanol permeability measurements

Conductivity measurements were carried out on Q-PVA/PECH anion-exchange composite membranes using an AC impedance method. The Q-PVA/PECH composite samples were immersed in a 4 M KOH solution for 24 h before measurement. Alkaline Q-PVA/PECH composite polymer membranes were clamped between SS304 stainless steel and ion-blocking electrodes, each of surface area 1.32 cm^2, in a spring-loaded glass holder. A thermocouple was kept in close proximity to the composite polymer membrane for temperature measurement. Each sample was equilibrated at the experimental temperature for at least 30 min before measurement. AC impedance measurements were carried out using an Autolab PGSTAT-30 (Eco Chemie B.V., Netherlands). The AC spectra in the range of 300 kHz–10 Hz at an excitation signal of 10 mV were recorded. AC impedance spectra of the anion-exchange composite polymer membrane were recorded at a temperature range between 30 and 70 °C. Experimental temperatures were maintained within ± 0.5 °C by a convection oven. All Q-PVA/PECH anion-exchange composite polymer electrolytes were examined at least in triplicate.

Methanol permeability measurements [20, 21] were conducted using a diffusion cell. The cell was divided into two compartments, in which one compartment was filled with D.I. water (called compartment B) and the other compartment filled with a 20 wt% methanol aqueous solution (called compartment A). Prior to testing, all Q-PVA/PECH composite polymer membranes were hydrated in D.I. water for at least 24 h. The composite polymer membrane with a surface area of 0.58 cm^2 was sandwiched by *O*-ring and clamped tightly between two compartments. The glass diffusion cell was kept stirring during the experiment. The concentration of methanol diffused from compartment A to B across the Q-PVA/PECH composite polymer membrane was examined with time using a density meter (Mettler Toledo, DE45). A 0.20 mL aliquot was sampled from the compartment B every 30 min. Before the permeation experiment, a calibration curve for the value of density versus the methanol concentration was prepared. The calibration curve was used to calculate the methanol concentration in the permeation experiment. The methanol permeability was calculated from the slope of the straight-line plot of methanol concentration versus permeation

time. The methanol concentration in compartment B as a function of time is given in Eq. 3

$$C_B(t) = \frac{A}{V}\frac{DK}{L}C_A(t - t_o) \quad (3)$$

where C is the methanol concentration, A and L are the composite polymer membrane area and thickness; D and K are the methanol diffusivity and partition coefficient between the membrane and the solution. The product DK is the membrane permeability (P), and t_o, also termed time lag, is related to the diffusivity: $t_o = L^2/6D$.

2.5 Micro-Raman spectroscopy analyses, nitrogen content, and ion-exchange capacity (IEC)

Micro-Raman spectroscopy was applied to characterize pure PVA polymer, PECH polymer, and Q-PVA/PECH composite membranes. The micro-Raman spectroscopy analysis was carried out using a Renishaw confocal microscopy/Raman spectroscopy system having a microscope equipped with 10×, 20×, and 50× objectives, and a charge coupled device (CCD) detector. Raman excitation source was provided by a 632.8 nm He–Ne laser beam, which had a beam power of 17 mW, which was focused on the sample with a spot size of about 1 μm in diameter. The N content of the sample was analyzed using an elemental analyzer (Perkin Elmer EA 2400). The IEC, defined as mmol g^{-1}, was examined by using the standard back-titration technique [12, 13].

2.6 Preparation of the anode and cathode electrodes

The catalyst slurry ink for the anode was prepared by mixing 70 wt% PtRu black inks (Alfa, HiSPEC 6000, PtRu black with Pt:Ru = 1:1 at. ratio), 30 wt% PTFE binder solution (Du Pont, 60 wt% base solution), and a suitable amount of D.I. water and IPA. The resulting PtRu black mixtures were first ultrasonicated for 2 h. The PtRu black inks were loaded onto Ti-screen by an impregnation method [10] to achieve a loading of PtRu (1:1) black of 4 mg cm^{-2}. The as-prepared PtRu anode was dried in a vacuum oven at 110 °C for 2 h.

The carbon slurry for the gas diffusion layer of the air cathode was prepared with a mixture of 70 wt% Shawinigan acetylene black (AB50) with specific surface area of 80 m^2 g^{-1} and 30 wt% PTFE solution (Teflon-30 suspension) as a wet-proofing agent and binder. The carbon slurry was coated on a Ni-foam current collector and then pressed to 100 kg_f cm^{-2}. The gas diffusion layer was then sintered at temperature of 360 °C for 30 min. The catalyst layer of the air cathode was then prepared by spraying a mixture of a 15 wt% of PTFE solution binder and 85 wt% of mixed powders consisting of MnO_2 catalyst mixed with BP2000 carbon black (MnO_2:BP2000 = 1:1). The Ni-foam current collector was 1 × 1 cm^2. The detailed preparation method for the air electrodes has been reported in literature [1].

2.7 Electrochemical measurements

The Q-PVA/PECH composite polymer membrane was sandwiched between the sheets of the anode and the cathode, and then pressed to 100 kg_f cm^{-2} at 25 °C for 10 min to form a membrane electrode assembly (MEA). The electrode area of the MEA was about 1 cm^2.

The electrochemical measurements of alkaline DMFC were carried out in a two-electrode system. AC spectra of the ADMFC with the frequency range from 100 kHz to 0.01 Hz at an excitation signal of 5 mV were examined at OCP. The *E–t* curves of the ADMFC comprised the Q-PVA/PECH composite polymer membrane were recorded at varied current densities (10–150 mA cm^{-2}) using a 4 M KOH + 2 M CH_3OH fuel at 25 °C. The polarization (I–V) and the power density curves of the ADMFC were obtained using the same fuel and temperature at a scan rate of 1 mV s^{-1}. All electrochemical measurements were performed on an Autolab PGSTAT-30 electrochemical system with GPES 4.8 package software (Eco Chemie, The Netherlands). The electrochemical performance of the ADMFCs comprising of QPVA and Q-PVA/PECH SPEs with the cathode open to atmospheric air were systematically studied and compared in 4 M KOH + 1–4 M methanol fuels under ambient conditions [1].

3 Results and discussion

3.1 Thermal analyses

Figure 2 shows TGA curves of pure PVA film, QPVA film, and the Q-PVA/PECH (5:1) composite film. A TGA curve of pure PVA film shows three major weight loss regions. The first region at a temperature of 80–130 °C ($T_{max,1}$ = 89.1 °C) was due to the evaporation of free and bound water; the weight loss of the membrane was about 5–6 wt%. The second transition region at around 240–310 °C ($T_{max,2}$ = 264 °C) was due to the degradation of the PVA polymer film; the total weight loss at this stage was about 60–70 wt%. The peak of the third stage at around 410–460 °C ($T_{max,3}$ = 439 °C) was due to cleavage of the backbone of PVA polymer film; the total weight loss was about 94.63 wt% at 600 °C.

Figure 2 also shows DTG curves of the QPVA film, which also shows three major weight loss regions. The QPVA film, the first region at a temperature of 80–150 °C ($T_{max,1}$ = 89.2 °C) was due to the evaporation of free and bound water or the chemical degradation of graft

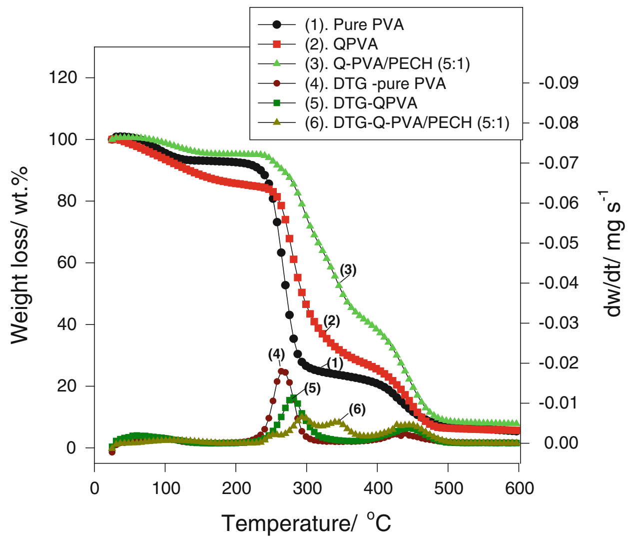

Fig. 2 TGA curves for pure PVA film, QPVA film, and Q-PVA/PECH (5:1) SPEs

quaternized groups; the weight loss of the membrane was about 6–7 wt%. The peak of second stage at around 250–320 °C ($T_{max,2}$ = 270 °C) was due to the degradation of the PVA polymer membrane. The peak of third stage at 410–470 °C ($T_{max,3}$ = 445 °C) was due to cleavage of the C–C backbone of QPVA polymer membranes; the total weight loss reached about 94.33 wt% at 600 °C.

Moreover, the TGA curve of Q-PVA/PECH (5:1) composite polymer membrane also revealed four major weight loss regions, which appeared as three peaks in the DTG curves. The first region at a temperature of 80–150 °C ($T_{max,1}$ = 110 °C) was also due to the evaporation of free and bound H_2O or the chemical degradation of graft quaternized groups; the weight loss of the membrane is ~1 wt%. The peak of the second stage at around 220–310 °C ($T_{max,2}$ = 290 °C) was also due to the degradation of Q-PVA/PECH polymer membrane. The peak of the third stage at 320–380 °C ($T_{max,3}$ = 350 °C) was due to cleavage of the C–Cl bond in PECH polymer; the total weight loss was only approximately 50.3 wt% at 600 °C. The peak of the fourth stage at 400–500 °C ($T_{max,4}$ = 460 °C) was due to cleavage of the C–C backbone of Q-PVA/PECH polymer membrane; the total weight loss was approximately 92.2 wt% at 600 °C.

As we know, the peak temperature or the maximum temperature (T_{max}) represents the fastest rate of the thermal decomposition stage. It is seen that the $T_{max,2}$, i.e., $T_{max,PVA}$ = 270 °C, for QPVA is due to the fastest degradation rate of the QPVA polymer membrane. However, the $T_{max,2}$, i.e., $T_{max,PVA}$ = 290 °C, and $T_{max,3}$, i.e., $T_{max,PECH}$ = 350 °C, for Q-PVA/PECH (5:1) is due to the fastest degradation rate of the PVA and PECH polymers, respectively. $T_{max,PVA}$ is increased from 270 °C to 290 °C after the PECH is blended.

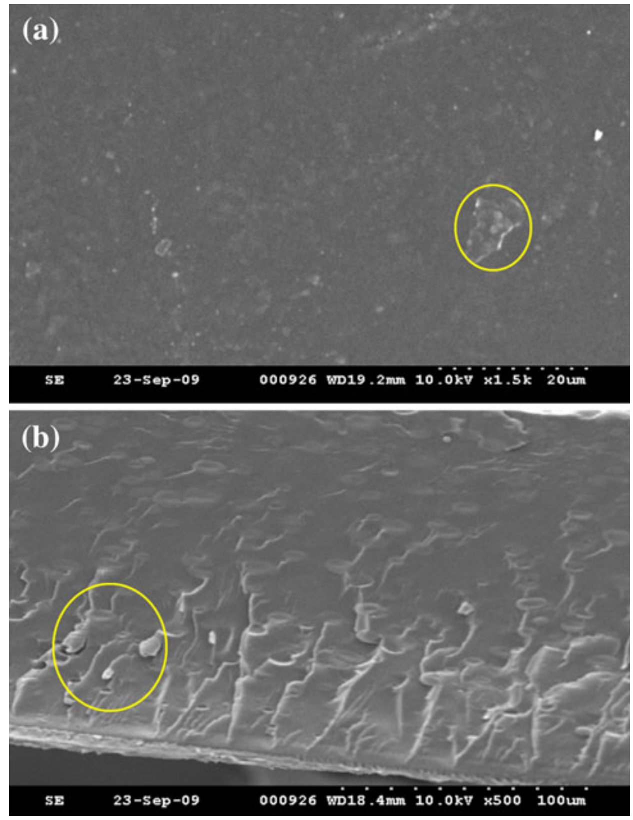

Fig. 3 SEM photographs for the Q-PVA/PECH (5:1) SPE: **a** top-view; **b** cross-section view

Also $T_{max,PECH}$ (350 °C) is much higher than $T_{max,PVA}$ (290 °C); indicating much good thermal stability for Q-PVA/PECH composite polymer membranes.

Overall, the degradation peaks of crosslinked Q-PVA/PECH composite polymer membranes are less intense and shift toward higher temperatures. It can be concluded that the thermal stability is improved due to the addition of PECH polymer and the chemical cross-linking reaction between PVA and GA.

3.2 Surface morphology and crystal structure

SEM images of the top and cross-section views for the Q-PVA/PECH (5:1) composite polymer membranes are shown in Fig. 3a and b, at a magnification of 1500× and 500×, respectively. It was revealed that the surface morphology of the Q-PVA/PECH composite polymer sample is not smooth, which shows some aggregates or chunks that are distributed on the top surface. It was found that the dimension of those undissolved PECH polymers (white color) or aggregates embedded in PVA matrix was about 0.1–5 μm. The results also indicate that the PECH polymers tend to form aggregates (forming a big chunk) that cause a non-uniform morphology, as seen clearly in Fig. 3b

for the cross-sectional view for Q-PVA/PECH composite polymer film.

The soft PVA polymer and the stiff PECH polymer are slightly inhomogeneous, but without any phase separation when a suitable amount of PECH polymers are blended (i.e., PVA:PECH = 5:1). The suitable amount of stiff PECH polymer is related to methanol permeation barrier performance. Its presence in the PVA polymer network assists in reducing methanol crossover through the composite polymer membrane.

The X-ray diffraction measurement was also performed to examine the nature of the crystallinity of the Q-PVA/PECH composite polymer membranes at varied compositions. Figure 4 shows the diffraction pattern for the QPVA polymer film and the Q-PVA/PECH composite polymer membranes. It is well known that the PVA polymer film usually exhibits a semi-crystalline structure with peaks at the 2θ angles of 19.90° and 40°. As can be seen clearly in Fig. 4, a peak at 2θ of 19.90° for the QPVA polymer film was seen. But, it was also clearly observed that the peak intensity of the Q-PVA/PECH composite polymer membranes greatly reduced as the PECH polymer was blended. It implies that the addition of PECH polymers into PVA polymer matrix greatly augmented the domain of amorphous region, i.e., the intensity of XRD crystal peak significantly decreases. It was seen that the Q-PVA/PECH

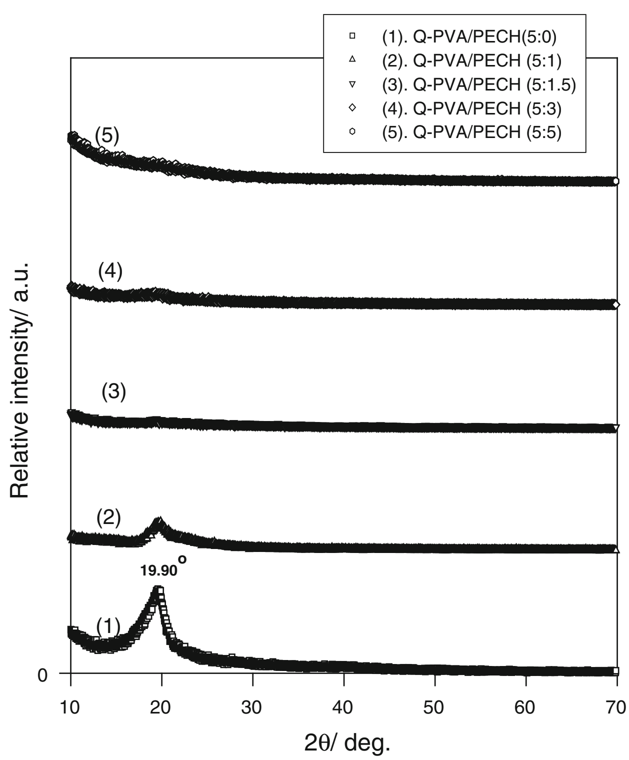

Fig. 4 XRD pattern for Q-PVA/PECH composite polymer membranes at varied compositions

(5:5) composite polymer membranes become totally amorphous. There is a significant motion of polymer chain in the amorphous domains or some defects and free volumes existing at the interface of between polymer chains while non-conducting in the crystalline phase. The characteristics of the Q-PVA/PECH composite polymer membranes show good ionic conductivity property. One is due to the formation of more amorphous domains facilitating the local PVA chain segmental motion in the Q-PVA/PECH composite polymer membrane. The other is due to the quaternized $–N^{+}Me_3$ groups grafting on the PVA and PECH side chains, i.e., amination, as seen in Fig. 1b.

3.3 Micro-Raman analyses

Figure 5a shows the micro-Raman spectra of GTMAC, PVA/5wt%GA, and QPVA/5wt%GA SPEs, respectively. There were several strong characteristic scattering peaks for GTMAC located at 760 (C–N stretch), 1,265, 1,447, and 1,479 cm^{-1}. In addition, there also were several strong characteristic scattering peaks for PVA/5wt%GA SPE located at 852, 918, 1,140, 1,440 cm^{-1}. As a results, there also were several strong characteristic scattering peaks for QPVA/5wt%GA SPE located at 852, 918, 1,140, 1,440, and 1,479 (due to GTMAC) cm^{-1}. It can be observed from micro-Raman spectra that very strong two characteristic scattering peaks for PECH polymer are located at 707 and 743 cm^{-1}, as shown in Fig. 5b. In addition, there were also several main scattering peaks at 707, 743, 856, 914, 1,140, 1,443 cm^{-1} for the PVA/PECH (5:1) SPE, as displayed in Fig. 5b. For comparison, two additional strong peaks at 707 and 743 cm^{-1} did not appear obviously on the Q-PVA/PECH (5:1) SPE, as compared to the Raman peaks of PVA/PECH (5:1) SPE. The peaks at 707 and 743 cm^{-1} were due to the C–Cl stretching for the PECH polymer. It was found that all intensities of Raman peaks in the Q-PVA/PECH (5:1) SPE were much lower than those of PVA/PECH SPE. It was found that the major Raman peaks of PVA were shifted to higher wave-number positions, which indicated a number of interactions occurred between PVA and PECH. Table 1 lists in detail a number of major Raman peak positions for pure GTMAC, PVA/5wt%GA, QPVA/5wt%GA, PVA/PECH (5:1)/5wt%GA, and Q-PVA/PECH (5:1)/5wt%GA composite polymer membrane for comparison.

3.4 Ionic conductivity and methanol permeability measurements

The typical AC impedance spectra of Q-PVA/PECH (5:1) anion-exchange composite membrane at different temperatures are shown in Fig. 6. The AC spectra were typically non-vertical spikes for stainless steel (SS) blocking

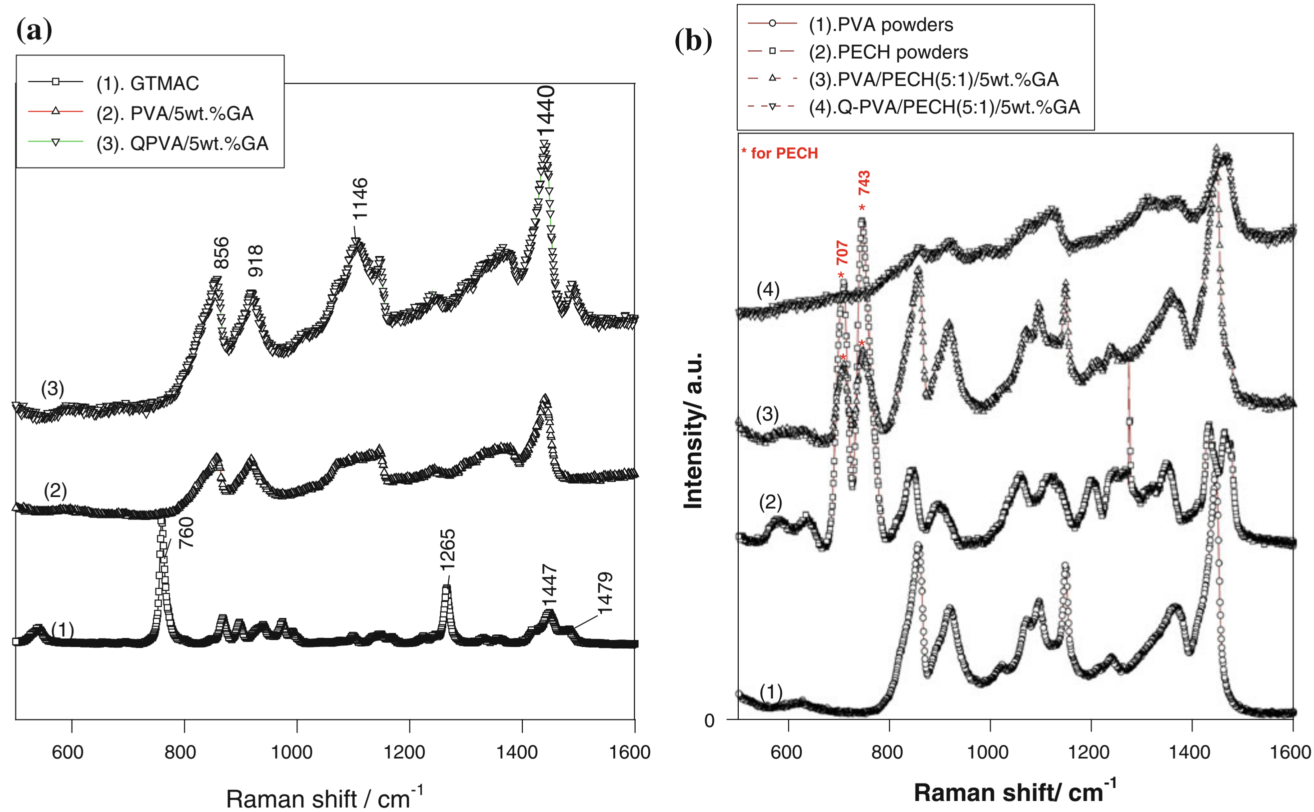

Fig. 5 Micro-Raman spectra for **a** GTMAC, PVA/5wt%GA, and QPVA/5wt%GA; **b**. PVA powders, PECH, PVA/PECH (5:1)/5wt%GA, and Q-PVA/PECH (5:1)/5wt%GA SPEs

Table 1 Micro-Raman peak positions for PECH, pure PVA, and Q-PVA/PECH composite polymer membrane

Types of films	Peaks						
	Major peak positions/cm^{-1}						
GTMAC	760	1,265				1,447	1,479
PECH	707	743					
PVA	–	–	852	918	1,140	1,440	
QPVA	760 (minor)		852	918	1,146	1,440	
PVA/PECH	707	743	856	914	1,140	1,443	
Q-PVA/PECH	–	–	856	914	1,140	1,443	

electrodes, i.e., the SS\Q-PVA/PECH SPE\SS cell. Analysis of the spectra yielded information about the properties of alkaline Q-PVA/PECH composite polymer electrolyte, such as bulk resistance, R_b. Taking into account the thickness of the composite electrolyte films, the R_b value was converted into the ionic conductivity value, σ, according to the equation: $\sigma = L/R_bA$, where L is the thickness (cm) of Q-PVA/PECH polymer membrane, A is the area of the blocking electrode (cm^2), and R_b is the bulk resistance (ohm) of the alkaline composite polymer membrane.

Typically, the R_b values of alkaline Q-PVA/PECH anion-exchange composite polymer electrolytes are on the order of 0.21–0.28 ohm and are dependent on the quantitative content of the PECH polymer, the degree of quaternization, and concentration of KOH. Note that the composite polymer membrane was dipped in a 4 M KOH solution for 12 h before performing measurements.

Table 2 lists the ionic conductivities of pure PVA film, QPVA, PVA/PECH, Q-PVA/PECH (5:1), and Q-PVA/PECH (5:5) composite polymer electrolytes with 4 M KOH electrolyte at different temperatures. As a result, the ionic conductivity value for pure PVA polymer membranes is 0.0106 S cm^{-1} at 30 °C. Comparatively, the ionic conductivity values of alkaline PVA/PECH (5:1), Q-PVA/PECH (5:1), and Q-PVA/PECH (5:5) composite polymer electrolytes, after being dipped in 4 M KOH solution, are 0.0219 and 0.0558, and 0.0088 S cm^{-1} at 30 °C,

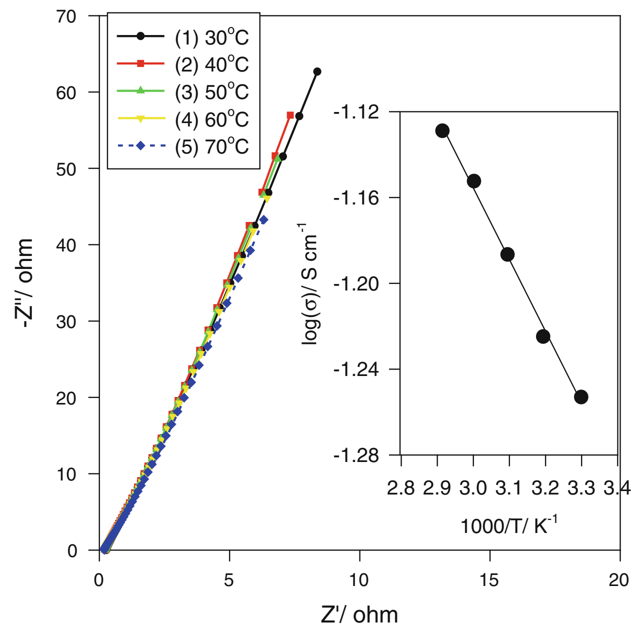

Fig. 6 Nyquist and Arrhenius plots (the inset) for the QPVA/PECH (5:1) SPE containing with 4 M KOH electrolyte

respectively. It shows that the Q-PVA/PECH (5:1) composite polymer electrolyte, for which $\sigma = 0.0558$ S cm^{-1} at ambient temperature, shows the highest ionic conductivity. It was also found that the ionic conductivity of the Q-PVA/PECH (5:1) polymer membrane ($\sigma_{30\,°C} = 0.0558$ S cm^{-1}) being quaternized by GTMAC was greatly increased, as compared with the PVA/PECH polymer membrane without any quaternized treatment ($\sigma_{30\,°C} = 0.0219$ S cm^{-1}) [16]. This may be due to the effect of the quaternization process or amination treatment. Some quaternized ammonium of GTMAC was grafted onto the PVA and PECH polymer chains; those ionic groups (–$N^{+}Me_3$ groups) could greatly enhance the ionic conductivity of the Q-PVA/PECH composite membranes. In general, the PVA/PECH polymer membrane did not contain any ionic groups on the polymer PVA polymer matrix; therefore, it shows a lower value of ionic conductivity.

Moreover, the ionic conductivity of Q-PVA/PECH (5:1) composite polymer electrolyte ($\sigma_{30\,°C} = 0.0558$ S cm^{-1}) was much higher than that of Q-PVA/PECH (5:5) composite polymer electrolyte ($\sigma_{30\,°C} = 0.0088$ S cm^{-1}). This may be due to the poor compatibility (a phase separation occurred) between the PVA polymer and the PECH polymer when the weight ratio of PVA:PECH is 5:5. Table 3 also displays the ionic conductivities of pure PVA film, QPVA, PVA/PECH, Q-PVA/PECH (5:1), and Q-PVA/PECH (5:5) composite polymer electrolytes in water at different temperatures. It was shown clearly that the ionic conductivity value of pure PVA film is of the order of 10^{-5} S cm^{-1}; however, the ionic conductivity values are 10^{-3} S cm^{-1} for QPVA and Q-PVA/PECH anion-exchange composite polymer membranes.

According to the ionic conductivity results, it is clearly seen that the ionic conductivity of Q-PVA/PECH composite polymer electrolytes increases when the PVA/PECH SPE was put through a quaternization process. As expected, since the PECH polymer used is a stiffer material in the PVA matrix, the methanol crossover and swelling ratio of the composite polymer membranes were reduced (data shown

Table 2 Ionic conductivities (S cm^{-1}) for pure PVA, PVA/PECH, QPVA, and Q-PVA/PECH anion-exchange composite membranes containing 4 M KOH electrolyte at various temperatures

Temp.	σ/S cm^{-1}				
	Pure PVA	QPVA	PVA/PECH (5:1)[a]	Q-PVA/PECH (5:1)	Q-PVA/PECH (5:5)
30 °C	0.0106	0.0217	0.0219	0.0558	0.0088
40 °C	0.0112	0.0233	0.0233	0.0596	0.0144
50 °C	0.0131	0.0258	0.0238	0.0651	0.0175
60 °C	0.0152	0.0285	0.0248	0.0700	0.0198
70 °C	0.0182	0.0308	0.0254	0.0743	0.0211

[a] Data obtained from Ref. [16] without any amination treatment

Table 3 Ionic conductivities (mS cm^{-1}) for pure PVA, QPVA and Q-PVA/PECH anion-exchange composite membranes containing water at various temperatures

Temp.	σ/mS cm^{-1}			
	Pure PVA	QPVA	Q-PVA/PECH (5:1)	Q-PVA/PECH (5:5)
30 °C	0.0386	0.88	1.30	1.15
40 °C	0.0539	1.13	1.57	1.38
50 °C	0.0686	1.49	1.94	1.72
60 °C	0.0838	1.90	2.38	2.11
70 °C	0.0982	2.20	2.74	2.33

Table 4 The liquid update and swelling ratio for pure PVA and Q-PVA/PECH anion-exchange composite polymer membranes

Films compositions	Values			
	D.I. water		99 wt% CH_3OH	
	S%	*A%*	*S%*	*A%*
PVA/PECH (5:1)	90	445	9.2	11.5
Q-PVA/PECH (5:1)	88	315	8.2	10.1
Q-PVA/PECH (5:3)	69	232	7.5	9.0
Q-PVA/PECH (5:5)	61	154	6.7	8.01

Table 5 The N content (%) of pure PVA, QPVA, PVA/PECH, and the Q-PVA/PECH composite polymer membranes

Samples	Avg. N/%	IEC/meq g^{-1}
Pure PVA	0.00 ± 0.02	0.03 ± 0.005
QPVA	1.17 ± 0.03	0.41 ± 0.02
PVA/PECH (5:1)	0.02 ± 0.01	0.02 ± 0.003
Q-PVA/PECH (5:1)	1.02 ± 0.03	0.64 ± 0.03
Q-PVA/PECH (5:3)	0.91 ± 0.02	0.45 ± 0.02
Q-PVA/PECH (5:5)	0.80 ± 0.02	0.40 ± 0.03

later). As expected, the thermal properties, ionic conductivity, and methanol crossover rates were all improved.

However, the ionic conductivity of Q-PVA/PECH composite polymer electrolytes starts to decrease when the weight ratio of PVA:PECH is 5:5. The $\log_{10}(\sigma)$ versus $1/T$ plot, as shown in the inset of Fig. 6, shows the derived activation energy (E_a) of the Q-PVA/PECH (5:1) anion-exchange composite polymer membrane, which is highly dependent on the amount of the KOH electrolyte in the Q-PVA/PECH matrix. In addition, the E_a value of the Q-PVA/PECH composite polymer membranes is on the order of ca. 6 kJ mol^{-1}.

Furthermore, the permeability measurements for methanol were also carried out with Q-PVA/PECH composite polymer membranes. All values of methanol permeability for Q-PVA/PECH composite polymer membranes were obtained from the slope of the straight line (also see references of [1]). It is shown that the methanol permeability values of the Q-PVA/PECH composite polymer membrane are 4.60×10^{-7}–2.52×10^{-7} cm^2 s^{-1}, at 25 °C. It was observed that the methanol permeability value of the Q-PVA/PECH composite polymer membrane (on the order of 10^{-7} cm^2 s^{-1}) is much lower than that of Nafion membrane (on the order of 10^{-6} cm^2 s^{-1}).

3.5 Liquid uptake and swelling ratio and IEC

Besides, the dimension stability of the Q-PVA/PECH composite polymer membrane is also very important for a practical DMFC application. The results of the liquid uptake ($A\%$) and swelling ratio ($S\%$) for the Q-PVA/PECH composite polymer membrane in D.I. water and 99% CH_3OH are shown in Table 4. As seen in Table 4, the liquid uptake ($A\%$) of D.I. water for the QPVA/PECH composite polymer membrane decreases from 445 to 154% as the composition of PVA: PECH polymer increases from 5:1 to 5:5. However, the $A\%$ and $S\%$ for the un-quaternized and quaternized PVA/PECH (5:1) composite polymer membranes were also listed in Table 4 for comparison. It was found that the water liquid uptake of un-quaternized PVA/PECH (5:1) composite polymer membrane (445%) is much higher than that of quaternized PVA/PECH (5:1) composite polymer membrane (315%). Furthermore, the swelling ratio ($S\%$) for the Q-PVA/PECH composite polymer membrane in D.I. water decreases from 88 to 61% when the composition of PVA: PECH polymer increases from 5:1 to 5:5. As we know, when the PECH polymer used as a stiffer material is added to the soft PVA matrix, the swelling ratio of the Q-PVA/PECH composite polymer membrane is reduced. The dimension stability and swelling properties are indeed improved. The methanol uptake for all Q-PVA/PECH composite polymer membranes is approximately 8–11%. Interestingly, it was found that the methanol uptake of un-quaternized PVA/PECH (5:1) composite polymer membrane (11.5%) is much higher than that of quaternized PVA/PECH (5:1) composite polymer membrane (10.1%).

The nitrogen (N) content in the composite polymer membrane was analyzed using an elemental analyzer (EA), yielding a range of 0.80–1.02% for the Q-PVA/PECH composite polymer membranes. However, the level is highly dependent on the content of the PECH polymers, as shown in Table 5. The N content generally decreases with the increase of the amount of PECH polymer added. The ionic conductivity of the Q-PVA/PECH composite polymer membranes also increased in conjunction with the N content in the samples. Table 5 lists the IEC values for the Q-PVA/PECH composite polymer membranes, which varied from 0.40 to 0.64 meq g^{-1}. The value of IEC is positively correlated with that of ionic conductivity in the samples.

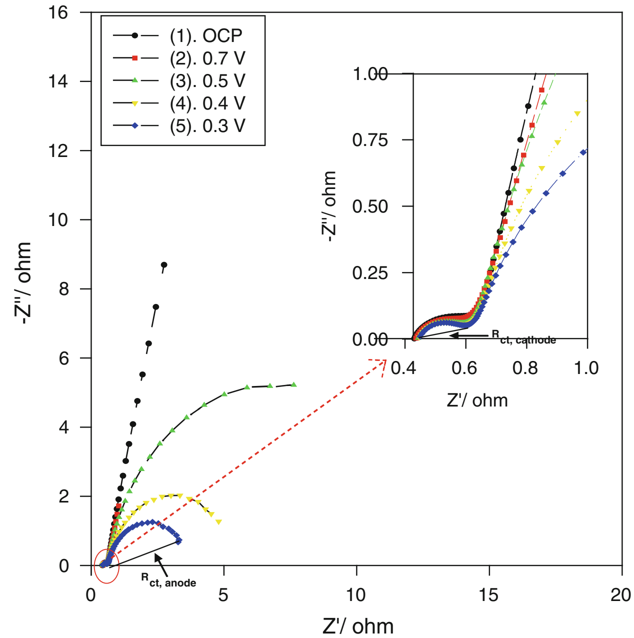

Fig. 7 AC spectra for the ADMFC comprised Q-PVA/PECH (5:1) SPE with a 4 M KOH + 2 M CH_3OH fuel at various cell voltages

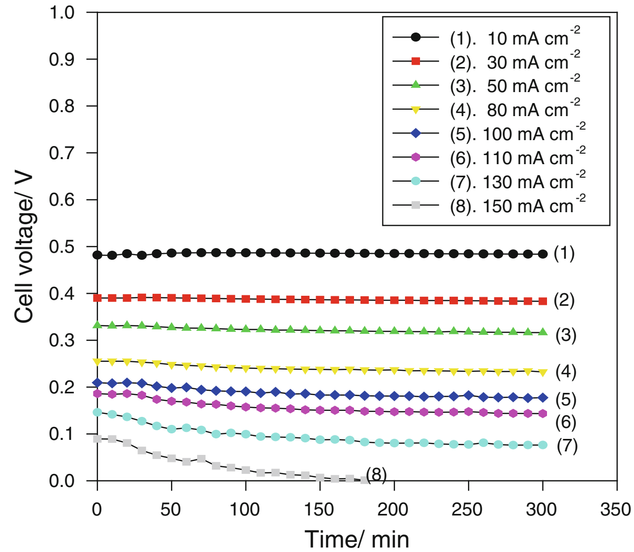

Fig. 8 The E–t curves for the ADMFC comprised the Q-PVA/PECH (5:1) SPE with a 4 M KOH + 2 M CH_3OH fuel at varied current densities

3.6 Electrochemical measurements

The AC impedance spectra for the DMFC employing the Q-PVA/PECH (5:1) composite polymer membrane with a 4 M KOH + 2 M CH_3OH solution fuel at open circuit potential (OCP) and varied cell potentials are shown in Fig. 7. The AC bulk resistance (R_b) is around 0.43–0.44 ohm, as seen more clearly in the inset of Fig. 7.

The value of the activation polarization resistance of the air cathode ($R_{ct,cathode}$, or $R_{ct,1}$) almost remained constant, around 0.20–0.26 ohm at varied potentials. However, the values of activation polarization resistance of the PtRu anode ($R_{ct,anode}$, or R_{ct2}) was markedly decreased from 14.48 to 3.11 ohm when the cell potential was reduced from 0.92 (E_{OCP}) to 0.30 V.

The E–t curves for the DMFC with a 4 M KOH + 2 M CH_3OH solution fuel at 25 °C at various constant current densities (from 10–150 mA cm^{-2}) for 300 min are shown in Fig. 8. It was observed that the best galvanostatic discharge performance (in terms of power density—P.D.) was at 100 mA cm^{-2} (P.D. = 21.40 mW cm^{-2}, E_{avg} = 0.210 V). By contrast, the poorest discharge performance was at 150 mA cm^{-2}. It was found that the cell voltage monotonically decayed and then dropped to zero after 180 min, as displayed in Fig. 8.

Figure 9a shows the cell voltage–current density and the power density–current density curves for alkaline DMFC with the QPVA SPE at various 4 M KOH + 1–4 M CH_3OH fuels at room temperature, respectively. As a result, the highest peak power density of 17.54 mW cm^{-2} for alkaline DMFC with a 4 M KOH + 4 M CH_3OH fuel was achieved at $E_{p,max}$ = 0.241 V with a peak current density ($i_{p,max}$) of 74.04 mA cm^{-2}, as listed in Table 6. On the other hand, the peak power density of alkaline DMFC with a 4 M KOH + 2 M CH_3OH fuel was 15.56 mW cm^{-2} at $E_{p,max}$ = 0.240 V with a peak current density of 65.13 mA cm^{-2} at 25 °C.

Comparatively, Fig. 9b show the cell voltage-current density and the power density- current density curves for alkaline DMFC with the Q-PVA/PECH (5:1) SPE at various 4 M KOH + 1–4 M CH_3OH fuels at room temperature. Consequently, the highest peak power density of 22.3 mW cm^{-2} for alkaline DMFC with a 4 M KOH + 2 M CH_3OH fuel was achieved at $E_{p,max}$ = 0.214 V with a peak current density ($i_{p,max}$) of 104.10 mA cm^{-2}, as listed in Table 7. On the other hand, the peak power density of alkaline DMFC with a 4 M KOH + 4 M CH_3OH fuel was 20.81 mW cm^{-2} at $E_{p,max}$ = 0.234 V with a peak current density of 88.95 mA cm^{-2} at 25 °C.

By comparison, the peak power density of the DMFC (P.D. = 22.30 mW cm^{-2}) comprised Q-PVA/PECH (5:1) SPE with the same fuel, 4 M KOH + 2 M CH_3OH, is much higher than that of the DMFC (P.D. = 9.25 mW cm^{-2}) comprised PVA/10wt%TiO_2 SPE [22]. This indicated that the electrochemical performance could be greatly improved (increase about 2.4 times) through a quaternization process of PVA-based composite polymer membrane [17–19]. More importantly, the ADMFC comprised Q-PVA/PECH composite polymer membrane with a 4 M KOH + 2 M CH_3OH fuel presented higher OCP (E_{ocp} = 0.923 V), which

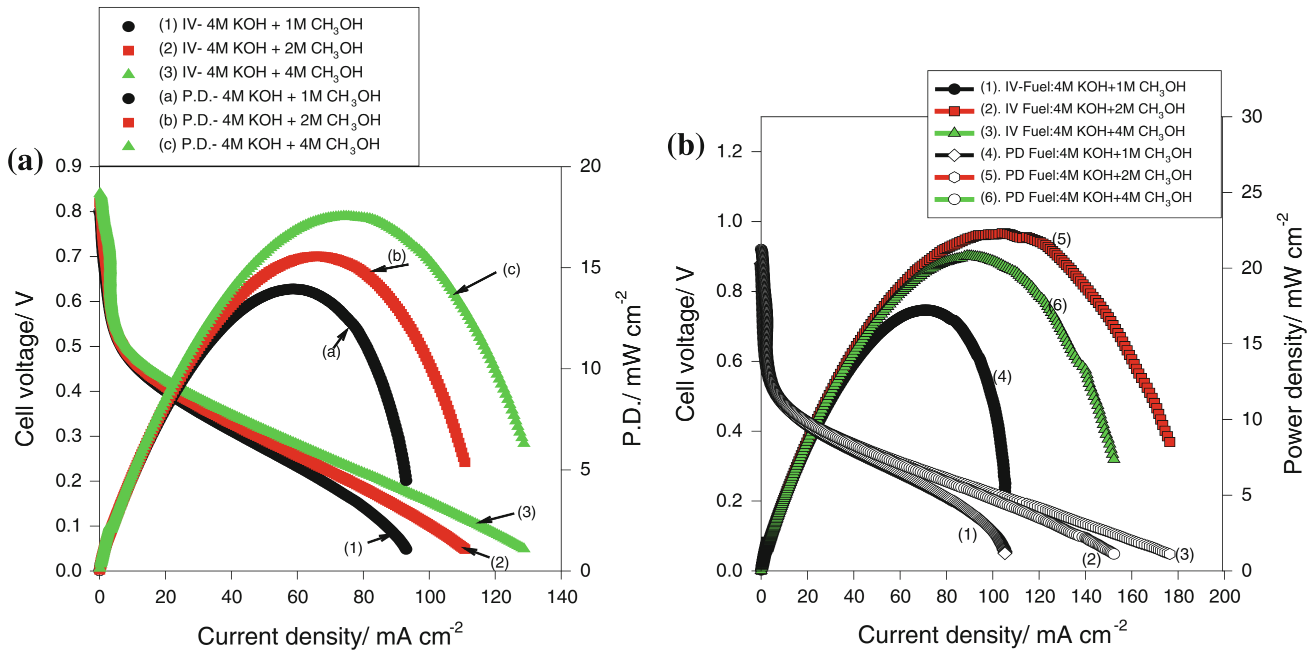

Fig. 9 The I–V and P.D. curves of the ADMFCs with: **a** QPVA SPE; **b** Q-PVA/PECH (5:1) SPE at various fuel compositions at 25 °C

Table 6 The OCP, I–V, and power density values of the ADMFC comprised QPVA electrolyte membrane with varied concentrations of methanol fuels

Parameters	Conc.		
	4 M KOH + 1 M CH_3OH	4 M KOH + 2 M CH_3OH	4 M KOH + 4 M CH_3OH
Max. P.D./mW cm^{-2}	13.95	15.56	17.54
$i_{p,max}$/mA cm^{-2}	59.08	65.13	74.04
$E_{p,max}$/V	0.240	0.240	0.241
E_{ocp}/V	0.840	0.820	0.830

Table 7 The OCP, I–V, and power density values for ADMFC comprised Q-PVA/PECH (5:1) composite electrolyte membrane with varied concentrations of methanol fuels

Parameters	Conc.		
	4 M KOH + 1 M CH_3OH	4 M KOH + 2 M CH_3OH	4 M KOH + 4 M CH_3OH
Max. P.D./mW cm^{-2}	17.22	22.30	20.81
$i_{p,max}$/mA cm^{-2}	70.95	104.10	88.95
$E_{p,max}$/V	0.243	0.214	0.234
E_{ocp}/V	0.910	0.923	0.890

indicated less methanol permeability and it showed much better electrochemical performance [1, 2].

Furthermore, the lowest power density of the ADMFC with a 4 M KOH + 1 M CH_3OH fuel was 17.22 mW cm^{-2} at $E_{p,max} = 0.243$ V, with a peak current density of 70.95 mA cm^{-2} at 25 °C. In fact, the values of peak power densities were also on the order of 4 M KOH + 2 M methanol>4 M KOH + 4 M methanol>4 M KOH + 1 M methanol. Especially, 4 M KOH + 2 M methanol solution fuel shows the highest power density (22.30 mW cm^{-2}) among these three methanol concentrations.

Table 8 presents a comparison of the peak power density values of alkaline DMFCs with x M KOH + 1–4 M CH_3OH fuels at various compositions alkaline polymer membranes, catalysts, and operating conditions as reported in the literature. This table shows that the electrochemical performances of ADMFCs with the composite polymer membranes could be improved greatly through quaternization [8–10] for the Q-PVA/PECH blend composite polymer. Our ADMFCs with Q-PVA/PECH (5:1) composite polymer electrolyte show comparable electrochemical performances, as compared with those ADMFCs with

Table 8 Comparison the electrochemical performances for various ADMFCs, in terms of P.D., at different preparation and operation conditions with varied KOH + CH_3OH fuels

Fuels	Anodes	Cathodes	Electrolyte membranes	*T*/°C	P.D.$_{max}$/mW cm^{-2}	Ref.
CH_3OH + NaOH	Pt/C	Pt/C	Morgane-ADP, Solvay	60	6.8	[9]
CH_3OH + KOH	PtRu/C	Pt/C	AHA Tokuyama	50	6.2	[24]
EG + KOH (1 M)		Pt/C			9.5	
EG + KOH (3 M)		Ag/C			8.1	
4 M KOH + 1 M CH_3OH	PtRu black	MnO_2/C	PVA/20wt%m-Al_2O_3/5wt%GA	25	15.55	[25]
4 M KOH + 2 M CH_3OH					18.33	
4 M KOH + 4 M CH_3OH					18.98	
4 M KOH + 1 M CH_3OH	PtRu black	MnO_2/C	PVA/20wt%TMAPFS/5wt%GA	25	22.28	
4 M KOH + 2 M CH_3OH					26.09	
4 M KOH + 4 M CH_3OH					20.96	
CH_3OH + NaOH	Pt/Ti	Pt/C	Morgane-ADP, Solvay	60	7.8	[10]
CH_3OH + KOH	PtRu black	MnO_2/C	PVA/TiO_2	25	9.25	[25]
C_2H_5OH + KOH					8.0	
CH_3OH + KOH	PtRu black	MnO_2/C	PVA/HAP	25	11.48	[26]
CH_3OH + KOH	PtRu/C	Pt/C	AAEM, Tokuyama	20	6.8	[27]
4 M KOH + 1 M CH_3OH	PtRu black	MnO/C	Q-PVA/PECH (5:1 in wt. ratio)	25	17.22	This work
4 M KOH + 2 M CH_3OH					22.30	
4 M KOH + 4 M CH_3OH					20.81	

various anion-exchange composite polymer membranes at room temperature and ambient air.

Accordingly, it is also demonstrated here the benefits of an alkaline DMFC consisting of an air electrode using a non-precious metal catalyst, i.e., inexpensive MnO_2 [23] instead of expensive Pt. The metal oxide catalyst (MnO_2) is not only inexpensive but also more tolerant toward cross-over, and is active for the reduction of O_2 to OH^- in alkaline media. Another advantage of this studied system is that the QPVA/PECH composite polymer membrane is a cheap, non-perfluorosulfonated polymer membrane as compared to expensive Nafion membrane.

4 Conclusions

Quaternized composite polymer membranes based on PVA and PECH polymers were for the first time prepared by a solution casting method and a quaternization process. This research demonstrates that the ionic conductivity of the Q-PVA/PECH composite polymer membrane greatly increases through a quaternization process by using GTMAC. Alkaline direct methanol fuel cells comprised the Q-PVA/PECH composite polymer membrane were assembled and examined systematically. Among three methanol fuels, the highest peak power density of the DMFC was with a 4 M KOH + 2 M CH_3OH fuel, at 22.30 mW cm^{-2}. The peak power densities of the ADMFC were in the order of 4 M KOH + 2 M methanol >4 M KOH + 4 M methanol >4 M KOH + 1 M methanol. As a result, Q-PVA/PECH composite polymer membranes can be obtained through a simple blend process. The Q-PVA/PECH anion-exchange composite membrane appears to be a viable candidate for applications in alkaline DMFC.

Acknowledgments Financial support from the National Science Council, Taiwan (Project No: NSC-99-2221-E131-009-MY2) is gratefully acknowledged.

References

1. Yang CC (2007) J Membr Sci 288:51
2. Yang CC, Chiu SJ, Chien WC (2006) J Power Sources 162:21
3. Wang Y, Li L, Hu L, Zhuang L, Lu J, Xu B (2003) Electrochem Commun 5:662
4. Baglio V, Arico AS, Blasi AD, Antonucci V, Antonucci PL, Licoccia S, Traversa E, Fiory FS (2005) Electrochim Acta 50:1241
5. Panero S, Fiorenza P, Navarra MA, Romanowska J, Scrosati B (2005) J Electrochem Soc 152:A2400
6. Chang HY, Lin CW (2003) J Membr Sci 218:295
7. Xu C, Shen PK, Ji X, Zeng R, Liu Y (2005) Electrochem Commun 7:1305
8. Agel E, Bouet J, Fauvarque JF (2001) J Power Sources 101:267
9. Yu EH, Scott K (2004) J Power Sources 137:248
10. Yu EH, Scott K (2004) Electrochem Commun 6:361
11. Yu EH, Scott K, Reeve RW (2003) J Electroanal Chem 547:17
12. Varcoe JR, Slade RCT (2006) Electrochem Commun 8:839
13. Varcoe JR, Slade RCT, Yee ELH (2006) Chem Commun 13:1428
14. Varcoe JR, Slade RCT (2005) Fuel Cells 5:187
15. Danks TN, Slade RCT, Varcoe JR (2003) J Mater Chem 13:712
16. Yang CC, Lin SJ, Hsu ST (2003) J Power Sources 122:210

17. Xiong Y, Fang J, Zeng QH, Liu QL (2008) J Membr Sci 311:319
18. Xiong Y, Liu QL, Zhu AM, Huang SM, Zeng QH (2009) J Power Sources 186:328
19. Xiong Y, Liu QL, Zheng QG, Zhu AM (2008) J Power Sources 183:447
20. Bae B, Kim D (2003) J Membr Sci 220:75
21. Kim J, Kim B, Jung B (2002) J Membr Sci 207:129
22. Yang CC, Chiu SJ, Lee KT, Chien WC, Lin CT, Huang CA (2008) J Power Sources 184:44
23. Yang CC, Hsu ST, Chien WC, Shih MC, Chiu SJ, Lee KT, Wang CL (2006) Int J Hydrogen Energy 31:2076
24. Matsuoka K, Iriyama Y, Abea T, Matsuoka M, Ogumia Z (2005) J Power Sources 150:27
25. Yang CC, Chiu SJ, Chien WC, Chiu SS (2010) J Power Sources 195:2212
26. Yang CC, Lin CT, Chiu SJ (2008) Desalination 233:137
27. Yu EH, Krewer U, Scott K (2010) Energies 3:1499